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CONCERNING THE ROLE OF THE REACTIVITY
OF AN OXIDIZING GROUP IN THE COMBUSTION
OF EXPLOSIVE COMPOUNDS

A. E. Fogelzang, et al

Foreign Technology Division
Wright-Patterson Air Force Base, Ohio

9 November 1973

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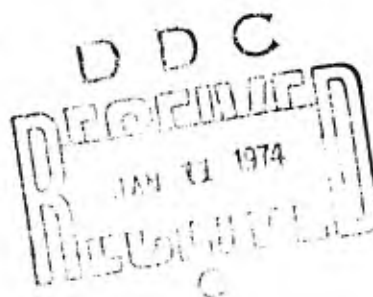
FOREIGN TECHNOLOGY DIVISION



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by

A. Ye. Fogel'zang, V. Ya. Adzhemyan,
B. S. Svetlov



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U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere.
 When written as ё in Russian, transliterate as yě or ě.
 The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

CONCERNING THE ROLE OF THE REACTIVITY OF AN
OXIDIZING GROUP IN THE COMBUSTION OF
EXPLOSIVE COMPOUNDS

A. Ye. Fogel'zang, V. Ya. Adzhemyan, and
B. S. Svetlov

It was shown earlier [1, 2], that explosive substances with the oxidizing agent Cl^{7+} burn almost by an order of magnitude faster than similar compounds with the oxidizing agent N^{5+} . It was possible to explain the higher combustion rate of perchlorates, both by the great reactivity of the oxidizing agent contained in the molecule, and by the improvement in the energy characteristics of the driving stage, since for them [3], in contrast to nitrocompounds [3-5], the reaction is not stopped by the products of incomplete combustion. Having investigated the combustion of compounds containing an active oxidizing agent in their molecule, but having a low heat of explosive transformation and vice versa, it is possible to explain, which of the factors has the main effect. As a model of such explosive substances salts were selected, the basis of the combustible in which were ammonia, methylamine, guanidine, and benzylamine, and the oxidizing agent - the inorganic acids (HMnO_4 ; HBrO_3 ; HIO_3 ; HIO_4 ; HClO_4 ; HClO_3 ; HNO_3 ; HNO_2 ; $\text{H}_2\text{Cr}_2\text{O}_7$; $\text{H}_2\text{Cr}_3\text{O}_{10}$).

The experiments were carried out in a constant-pressure bomb in accordance with the methodology described in [1]. The ammonium nitrite, chlorate, and trichromate were obtained in accordance with [6-8]. The ammonium iodate and bichromate were reagents of the "pure" grade, and the ammonium periodate was of the grade "for laboratory work." The ammonium permanganate was obtained from $(\text{NH}_4)_2\text{SO}_4$ and $\text{Ba}(\text{MnO}_4)_2$. The guanidine salts were prepared from a bicarbonate and an appropriate acid, and the methylamine and benzylamine salts were obtained from free amines. All the synthesized substances were recrystallized from water or alcohol and analyzed for acid content. The purity of the investigated products was 95-98%.

The dependences of $u_M(p)$ for the ammonium salts are presented in the table, from which it is evident, that a connection between the heat of combustion and the stability of the salt, on the one hand, and combustion rate, on the other hand -- is absent.

Actually, ammonium periodate burns considerably more rapidly than ammonium nitrite, in spite of the fact, that the former is more stable and has a lesser heat of reaction. The ammonium bichromate and trichromate burn at rates that are close to each other, although the heats of reaction for them differ almost by two times. At the same time, ammonium nitrite and bromate are close to each other with respect to combustion temperature and stability, however, the former burns approximately four times more slowly than the latter. However, if we arrange the salts in question in ascending order of activity of oxidizer contained in the molecule, than it is evident, that the combustion rate is higher, the more active is the oxidizing agent within the compound. Combustion rate sharply increases with an increase in the oxidizing potential (E_0). The detected connection, probably, is not accidental, since combustion is a typical oxidation-reduction reaction, and E_0 makes it possible to get an idea about the relative power of oxidizing agents. Let us note that the

Reactivity of oxidizing group during combustion.

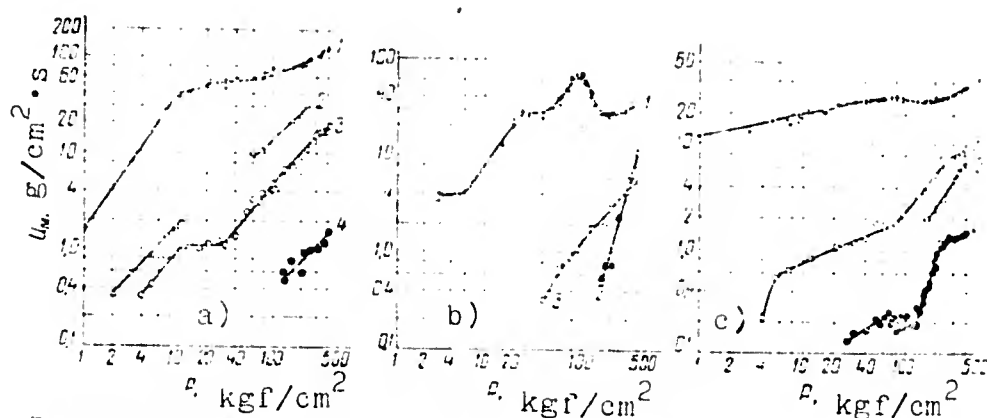
Sub- stance	p, at	$u_M(p)$, g/cm ² ·s	$T_{\text{всн}}$, °C	Q_p , kcal/kg [9]	$T_{\text{гop}}$, °K (calculation)	u_M (100 at), g/cm ² ·s	E_0 , V [13]
NH ₄ NO ₃	Does not burn up to 1000 at [10]		270	370 75*)	1200	—	NO/NO ₃ ⁻ 0.96
NH ₄ IO ₃	70—160	$9.3 \cdot 10^{-3} p^{0.92}$	150 [10]	75	750	0.65	I ₂ /IO ₃ ⁻ 1.19
	160—400	$3.6 \cdot 10^{-5} p^{2.0}$					
(NH ₄) ₂ Cr ₂ O ₇	20—60	$4.6 \cdot 10^{-1}$	240 [10]	300	1200	0.70	Cr ³⁺ /Cr ⁶⁺ 1.33
	60—400	$1.0 \cdot 10^{-2} p^{0.13}$					
(NH ₄) ₂ Cr ₂ O ₇	1—16	$1.4 \cdot 10^{-1} p^{0.53}$	190 [10]	165	850	0.76	Cr ³⁺ /Cr ⁶⁺ 1.33
	16—40	$1.3 p^{-0.3}$					
	40—100	$1.7 \cdot 10^{-2} p^{0.86}$					
	100—230	$2.6 \cdot 10^{-1} p^{0.3}$					
	230—400	$1.6 \cdot 10^{-3} p^{1.23}$					
NH ₄ ClO ₄	—	[12]	315 [10]	395	1450	2	Cl ₂ /ClO ₄ ⁻ 1.39
NH ₄ NO ₂	1—40	$6.0 \cdot 10^{-2} p^{1.14}$	90 [6]	825	1850	5.6	N ₂ /NO ₂ ⁻ 1.45
	40—200	$7.8 \cdot 10^{-1} p^{0.43}$					
	200—400	$5.5 \cdot 10^{-2} p^{0.91}$					
NH ₄ ClO ₃	1—9	$1.0 \cdot 10^{-1} p^{1.62}$	130 [10]	490	1650	8.6	Cl ₂ /ClO ₃ ⁻ 1.47
	9—20	$3.0 \cdot p^{0.10}$					
	30—400	$3.6 \cdot 10^{-1} p^{0.71}$					
NH ₄ IO ₄	1—5	$3.3 p^{0.63}$	~200	235**)	1150	22	IO ₃ ⁻ /IO ₄ ⁻ 1.51
	5—400	$8.4 p^{0.70}$		131			
NH ₄ BrO ₃	1—100	$1.1 \cdot p^{0.55}$	65—70 [11]	100	1900	24	Br ₂ /BrO ₃ ⁻ 1.52
NH ₄ MnO ₄	1—7	$p^{1.15}$	130 [10]	550	1400	58	MnO ₂ /MnO ₄ ⁻ 1.70
	7—400	$0.1 p^{0.34}$					

Note: The value with the asterisk - N⁵⁺ is reduced to NO; the two asterisks - I⁷⁺ is reduced to I⁵⁺ (I₂O₅).

dependence between E_0 and combustion rate extends over a broad pressure range for compounds investigated both in this work as well as in [1, 2]. Moreover, mixtures with more active oxidizing agents also burn in gases at a greater rate [15]. Thus, apparently, there is the possibility on the basis of the magnitude of the relative potential to predict the relative combustion rates of substances with different oxidizing agents and the same combustibles, since the reactivity of both the oxidizer and the combustible will determine the driving force. And, the simpler is the structure of the explosive compound, then, probably, the more accurately can this be done, since there are fewer possible directions for the course of the reaction.

We then investigated methylamine, guanidine, and benzylamine salts. It is evident from Figure (a), that approximately the same pattern is observed for methylamine salts, as for ammonium salts. Of four investigated salts the periodate burns with the greatest rate ($T_f = 2400^\circ\text{K}$). The combustion rate at 400 atm attains $120 \text{ g/cm}^2 \cdot \text{s}$. Methylamine nitrate burns more slowly than the other salts ($T_f = 1700^\circ\text{K}$). Perchlorate ($T_f = 3100^\circ\text{K}$) and iodate ($T_f = 1500^\circ\text{K}$) occupy an intermediate position. Let us note, that methylamine salts burn considerably more rapidly than ammonium salts.

The dependences $u_m(p)$ for guanidine and benzylamine salts are presented in the Figures (b, c). Periodic acid salts also burn here at a greater rate. Guanidine nitrate was incapable of combustion over the entire investigated pressure range ($T_f = 1400^\circ\text{K}$), and benzylamine nitrate burns more slowly than the other three salts. The certain difference in comparison with ammonium and methylamine salts, observed for guanidine and benzylamine perchlorates, apparently, is connected with the



Dependences of mass combustion rate on pressure for methylamine (a), guanidine (b), and benzylamine (c) salts: 1 - periodates; 2 - perchlorates (black triangles indicate combustion in the pulsating regime); (3) - iodates; 4 - nitrates.

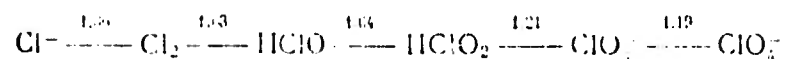
combustion characteristics of perchloric acid salts [1, 2, 12]:¹ the transition of combustion to the pulsating regime or the "discontinuities" on the curves of $u_m(p)$.

Thus, the noted very strong effect of oxidizing agent activity on the combustion rate of the investigated compounds makes it possible to assume, that the slowest process in combustion is an oxidation-reduction reaction, and the first state - the decomposition of the original substance - is tuned to its rate. Oxidation-reduction reactions proceed, as a rule, with less activation energy² as compared with decomposition reactions. Thus, probably, in switching from oxidizing agent to oxidizing agent, its activity, and not its combustion temperature is determinant with respect to rate.

¹Ammonium perchlorate at pressures above 150 at, when its combustion goes over to the pulsating regime, also drops out of the general sequence.

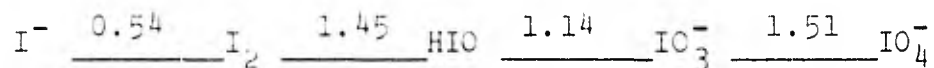
²If we examine ionic oxidation-reduction reactions in a solution or in a melt, then they have an activation energy close to zero.

It is interesting to compare the products formed after the combustion of a salt, with the variation in E_0 in the transition of an oxidizing agent from a higher level of oxidation to a lower level. Thus in the combustion of ammonium perchlorate at low pressures, one of the products is Cl_2 [3]. Perchlorates burn without a secondary flame. From an examination of the series:



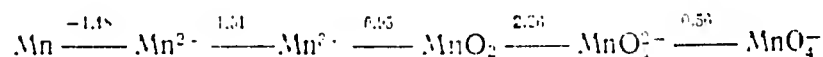
it is evident, that in reducing Cl^{7+} to Cl^- the activity of the products increase to Cl^+ , and then drops. However, Cl_2 is still a rather active oxidizer ($E_0 = 1.36$ V) and it, naturally, can readily enter into reaction with active reducing agents.

The pattern is different in the case of iodine:



Here, on the way from I^{7+} to I^- there is I^{5+} , which possesses weak oxidizing properties. Moreover, I_2 is a weak oxidizing agent. Actually, in the combustion of ammonium iodate at low pressures, one of the combustion products is I_2O_5 . Organic periodates burn with a secondary flame, upon the appearance of which in the range 30-150 at iodine is formed in the combustion products, which is absent in the low pressure range. A considerable quantity of I_2 crystals is always present in the products upon the combustion of iodates.

Upon the combustion of ammonium permanganate, manganese dioxide is formed, which, generally speaking, can be expected, if we examine the course of the reduction of Mn^{7+} :



Thus, having traced the variation in oxidizing potential in the course of the reduction of an oxidizer, it is possible, apparently, to predict the possibility of the appearance of a secondary flame or certain final reactions products.

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